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Vibrational spectra of 2,4- and 3,4-dimethyl phenols

B Singh* and R P Singh
Department of Physics, Jaglal Choudhary College, Chapra-841 301, Bihar, India

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Abstract The infrared and laser Raman spectra of 2,4- and 3,4-dimethyl phenols have been recorded The vibrational spectra have been analysed assuming C_s point group Assignments for fundamental vibrations, internal modes of vibration of CH_3 and OH groups and combination and overtone frequencies have been proposed

Keywords Raman spectra, infrared spectra, dimethyl phenol

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The vibrational spectra of p-nitro phenol in the region 300–1600 cm^{-1} have been studied by Jakobsen and Brewer [1]. Infrared spectra of o-, m- and p-nitro phenols have been studied by Yugal Kishore *et al* [2] Vibrational spectra of o-, m- and p-amino phenols have been studied by Verma and Rai [3] Vibrational spectra of 2,3- and 2,5-dimethyl phenols have been studied by Green *et al* [4]. The survey of the literatures indicates that no work have been reported on the vibrational spectra of 2,4- and 3,4-dimethyl phenols which will be termed *A* and *B* respectively hereafter.

The compounds *A* (in liquid state) and *B* (in solid state) were obtained from Koch Light Laboratories Ltd., England, in pure state and were used as such. The I.R. spectra of these compounds were recorded on double beam grating spectrophotometer PE983 in the range of 400–4000 cm^{-1} and the Raman spectra were recorded on Ramanor HG-2S (JOBIN-YUON, FRANCE) spectrophotometer in the range of 50 cm^{-1} to 4000 cm^{-1}.

A group of atoms acting as substituents (CH_3 and OH in the present case) may be treated as a single mass point, as the local symmetry of the benzene ring is not much affected by substituent group [5]. Assuming the planar structure, the compounds under consideration would belong to C_s point group and the 51(3N–6) normal modes of vibration may be classified as $35a' + 16a''$ Table 1 contains fundamental frequencies and internal modes of vibration of CH_3 and OH

Table 1. Fundamental frequencies of compounds *A* and *B* and internal modes of vibration of substituent groups

Species	Compound *A*		Compound *B*		Assignment
	I R	Raman	I R	Raman	
a'					
ν_1	–	3082(3 3) P		3080(1 6)	ν(C H)
ν_2	–	3052(3.8) P		3042(1.6)	ν(C–H)
ν_3	3020(5 5)	3028(4 0) P	3030(6 1)	3030(1.5)	ν(C–H)
ν_4	1610(6.0)	1613(4.9)	1610(5 0)	1610(1.8)	ν(C–C)
ν_5	1590(6 3)	1592(5 3) P	1590(4 8)	1587(1.7)	ν(C C)
ν_6	1510(2.0)	1503(4 5) P	1500(3 6)	1500(1 8)	ν(C–C)
ν_7	1410(4 9)	1415(4 5)	–	1425(1.8)	ν(C–C)
ν_8	1322(5.3)	1313(3 9)	1320(6 4)	1312(1 7)	ν(C–C)
ν_9	–	1295(3 9) P	1290(3 7)	1295(1 7)	ν(C–CH_3)
ν_{10}	1260(2 4)	1270(4 3) P	1260(4.1)	1265(1 8)	δ(C–H)
ν_{11}	1200(3.0)	1195(3 6) P	1205(4.5)	1197(1.8)	ν(C CH_3)
ν_{12}	1150(5 3)	1155(3 7) P	1155(3.9)	1155(1 7)	δ(C H)
ν_{13}	–	1085(3.5) P	–	1090(1.6)	δ(C H)
ν_{14}	–	958(3 1) P	950(6 3)	947(1.6)	ν(C–OH)
ν_{15}	780(4 6)	780(2 5) P	775(1.8)	772(2.9)	δ(C–C–C)
ν_{16}	555(8 9)	555(2.2) P	557(7.4)	555(1.9)	ν(C- C)
ν_{17}	490(6 5)	490(3.3) P	490(7.3)	492(1.9)	δ(C-C-C)

*Corresponding Author

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Table 1. *(Cont'd)*

Species	Compound *A*		Compound *B*		Assignment
	I.R	Raman	I R	Raman	
ν_{18}	–	465(1 9) P	-	475(2 5)	δ(C–C–C)
ν_{19}	n i.	353(2 2) P	n i.	345(2 0)	δ(C–CH_3)
ν_{20}	n i.	285(1 8) P	n i	280(1 8)	δ(C–CH_3)
ν_{21}	n i	265(1 6) P	n i	260(2 0)	δ(C–OH)
a''					
ν_{22}	930(6 4)	940(2 9) dp		930(1 9)	γ(C–H)
ν_{23}	875(6 5)	880(2 8) dp	867(6 1)	872(1 6)	γ(C–H)
ν_{24}	810(3 1)	810(2 5) dp	–	792(2 4)	γ(C–H)
ν_{25}	720(6 2)	717(2 8)	-	715(2 6)	γ(C–C–C)
ν_{26}	–	587(2 1) dp	–	585(1 8)	γ(C–C–C)
ν_{27}	445(5 4)	445(2 2)	447(6 3)	450(3 8)	γ(C–C–C)
ν_{28}	n i	222(2 3) dp	n i	220(9 6)	γ(C–CH_3)
ν_{29}	n i	212(2.2) dp	n i	205(2 8)	γ(C–CH_3)
ν_{30}	n i	150(2 1) dp	n i	155(2 4)	γ(C–OH)
CH_3 group vibrations					
a'					
ν_{31}	–	2990(2 6)	–	2990(1 7)	$\nu_{as}(CH_3)$
ν_{32}	–	2980(2 5)	2980(5 8)	2977(1 5)	$\nu_{as}(CH_3)$
ν_{33}	2960(4 3)	2955(2 9)	2950(5 3)	2960(1 6)	$\nu_{as}(CH_3)$
ν_{34}	–	2945(3 5)	–	2937(1 6)	$\nu_{as}(CH_3)$
ν_{35}	2920(3 3)	2915(7 2)	2930(5 1)	2925(1 5)	$\nu_s(CH_3)$
ν_{36}	–	2903(4.8)	–	2905(1 6)	$\nu_s(CH_3)$
ν_{37}		1645(4 2)	1460(4.7)	1462(1 8)	$\delta_{as}(CH_3)$
ν_{38}	1455(4 4)	1455(4 3)	–	1452(1 7)	$\delta_{as}(CH_3)$
ν_{39}		1440(4 2)	–	1445(1 7)	$\delta_{as}(CH_3)$
ν_{40}	–	1430(4 5)	1430(5 8)	1430(1 7)	$\delta_{as}(CH_3)$
ν_{41}	–	1385(4 8)	1380(6 7)	1382(1 8)	$\delta_s(CH_3)$
ν_{42}	1375(5 0)	1365(4 4)	1370(6 9)	1372(1 7)	$\delta_s(CH_3)$
a''					
ν_{43}	-	1070(3.7)	–	1065(1.8)	$\gamma_r(CH_3)$ Rocking
ν_{44}	1035(6 3)	1040(3 4)	–	1047(1 8)	$\gamma_r(CH_3)$
ν_{45}	1015(6 4)	1017(3 0)	1020(6.3)	1020(1 9)	$\gamma_r(CH_3)$
ν_{46}	1000(6 8)	1003(3 1)	1005(4 9)	1002(1 7)	$\gamma_r(CH_3)$
ν_{47}	n i	193(1 8)	n i	195(1.7)	$\gamma_t(CH_3)$ Twisting
ν_{48}	n i	170(1 8)	n i	175(1 9)	$\gamma_t(CH_3)$
OH group vibrations					
a'					
ν_{49}	–	3610(1 1)	3610(6 9)	3610(1 3)	ν(OH)
ν_{50}	–	1182(3 7)	–	1178(2 1)	δ(OH)
a''					
ν_{51}	n.i	304(1.7)	n.i	310(7.0)	γ(OH)

(ν = stretching, δ = in-plane bending, γ = out of plane bending, P = polarised, dp = depolarized, n i = not investigated, *as* = asymmetric, *s* = symmetric, *r* = rocking, *t* = twisting.

The figures in the brackets indicate intensity in the scale of 0 to 10. In Raman frequencies, the intensity of parallel positions has been given in the brackets

groups along with their proposed assignments. All the combinations and overtone frequencies along with their assignments have been given in Table 2. Assignments for the various observed frequencies have been made on the basis of intensity of infrared bands, the nature of polarization of Raman bands and the frequency range for different modes of similar molecules as given by Varsanyi [6,7].

Table 2. Combination and overtone frequencies (cm^{-1})

Compound (*A*)	Compound (*B*)
3225 = 1613 × 2 = 3226 (*A'*)	3580 = 3030 + 555 = 3585(*A'*)
2555 = 1613 + 940 = 2553 (*A'*)	3220 = 1610 × 2 = 3220(*A'*)
2230 = 1295 + 940 = 2235(*A''*)	2620 = 1312 × 2 = 2624(*A'*)
1945 = 1503 + 445 = 1948(*A''*)	2210 = 1500 + 715 = 2215(*A''*)
1750 = 1305 + 445 = 1750(*A''*)	1847 = 1500 + 345 = 1845(*A'*)
1220 = 780 + 445 = 1225(*A''*)	1782 = 1197 + 585 = 1782(*A''*)
905 = 555 + 353 = 908 (*A'*)	900 = 450 × 2 = 900(*A'*)
660 = 445 + 212 = 657 (*A'*)	750 = 492 + 260 = 752(*A'*)
422 = 2 × 212 = 424 (*A'*)	672 = 450 + 220 = 670(*A'*)

The frequencies ν_1, ν_2, ν_3 for *A* and *B* which lie in the region 3000–3100 cm^{-1} [6–8] have been assigned as ν(C–H), while the ν(C–X) (X = substituent) are mass dependent and have considerably reduced frequencies. The ν(C–X) frequencies are ν_9, ν_{11} and ν_{14} where the first two correspond to ν(C–CH_3) and the last one corresponds to ν(C–OH). The vibration modes 8*a*, 8*b*, 19*a*, 19*b*, 14 and 1 of benzene are ν(C–C). The frequency of the first five modes remain unchanged on substitution while the frequency of mode 1 changes on substitution. The frequency of normal mode 14 is not very sensitive to substitution and Varsanyi [6,7] has suggested a range for this mode between 1240–1290 cm^{-1}. However, it is important to note that this vibration is coupled in phenols with in-plane bending mode of the OH group resulting in an essential frequency increase [9]. The frequencies ν_4, ν_5, ν_6, ν_7, ν_8 and ν_{16} have been assigned as ν(C–C).

The δ(C–H) frequencies remain almost unaltered upon substitution but δ(C–X) frequencies decrease considerably The frequencies ν_{10}, ν_{12}, ν_{13} have been identified as three δ(C–H) and the frequencies ν_{19}, ν_{20}, ν_{21} have been assigned to δ(C–CH_3), δ(C–CH_3) and δ(C–OH) respectively. The frequencies ν_{15}, ν_{17}, ν_{18} have been assigned as δ(C–C–C). In benzene derivatives, the γ(C–H) vibrations are usually observed to lie in the range 700–1000 cm^{-1} and due to mass effect and other factors the frequency decreases considerably in γ(C–X) vibrations and frequencies below 350 cm^{-1} are to be assigned to γ(C–X) vibrations [6,7,10]. The frequencies

ν_{22}, ν_{23}, ν_{24} have been assigned as γ(C–H) while the frequencies ν_{28}, ν_{29}, ν_{30} have been assigned as γ(C–CH_3), γ(C–CH_3) and γ(C–OH) respectively. We have assigned ν_{25}, ν_{26}, ν_{27} as γ(C–C–C) and our assignments find support from the assignments proposed by earlier workers [1–4].

Each methyl group has three stretching vibrations, one being symmetric and the other two asymmetric. In the present case, four $\nu_{as}(CH_3)$ and two $\nu_s(CH_3)$ for two methyl groups have been observed at ν_{31}, ν_{32}, ν_{33}, ν_{34} and ν_{35}, ν_{36} respectively. Each methyl group has one symmetric, two degenerate asymmetric and two degenerate rocking modes of vibrations. Frequencies ν_{37}, ν_{38}, ν_{39}, ν_{40} have been assigned as $\delta_{as}(CH_3)$ while ν_{41}, ν_{42} have been assigned as $\delta_s(CH_3)$. The rocking vibrations $\gamma_r(CH_3)$ have been assigned at ν_{43}, ν_{44}, ν_{45}, ν_{46}. The CH_3 twisting modes have been assigned at ν_{47}, ν_{48}. The OH group has one stretching one in-plane bending and one out of plane bending frequencies. We have assigned ν_{49} in the range of 3500–3700 cm^{-1} [11] with sharp infrared band as ν(OH). We have assigned ν_{50} as δ(OH) and ν_{51} as γ(OH) for the present compounds

The moderately strong and weak bands at frequencies that could not reasonably be assigned to fundamentals may be combinations and overtones.

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